SULFUR ISOTOPIC SYSTEMATICS IN ALH84001. OPEN- AND CLOSED-SYSTEM BEHAVIOR OF SULFUR IN A MARTIAN HYDROTHERMAL SYSTEMS.

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INTRODUCTION. Understanding the development, timing, and setting of sulfides in fracture-filling lithologies in ALH84001 is critical to interpreting S isotopes as potential biomarkers in Martian samples. For example, to properly interpret S isotopes as a marker for biogenic activity [1], it is important to understand the relative sequence of pyrite-carbonate precipitation [2], the temperature of precipitation, and the open-closed system behavior of S species during precipitation. The latter is particularly important in evaluating the extent sulfate reducing bacteria will fractionate S isotopes. This abstract focuses upon the effect of open-closed system behavior of S species on S isotopic systematics in the system represented by ALH84001. Another abstract [2], focuses upon the precipitation history of carbonates and sulfides.

APPROACH. Shearer et al. [1] measured the sulfur isotopes in large pyrite grains (10 to 40 μm) associated with the carbonate fracture-filling lithologies in ALH84001. The $\delta^{34}S$ value for these pyrite ranged from 4.8 to 7.8 per mil. If a bacteria colony flourished at the time of pyrite precipitation, under what conditions will biogenic activity of sulfate-reducing bacteria be reflected in the sulfur isotopic signature of the sulfides? Will differences in the relative size of precipitating sulfides and bacteria influence the biogenic record registered in the sulfides [3]? This preliminary modeling of hypothetical martian biogenic fractionation of sulfur, used previous proposed models for terrestrial sulfur isotope fractionation in bacterial reduction processes [4,5,6,7]. The following assumptions were made for both open and closed system modeling: (1) Pyrite precipitated during bacterial activity. (2) Temperatures of precipitation were below 100° C. (3) Martian bacteria thought to be represented in ALH84001 processed sulfur in the same manner as terrestrial sulfate-reducing bacteria in that kinetic isotopic effects (k_1/k_2) are similar. (4) The $\delta^{34}S$ of solutions that carried sulfate to the site of precipitation was 0 per mil. (5) Sulfate reduction represented by the pyrite has not been modified by diagenetic processes. The preliminary modeling involved three types of martian systems: systems open to SO_4^{-2}, systems closed to SO_4^{-2} and H_2S, and systems closed to SO_4^{-2} and open to H_2S.

DISCUSSION. Martian systems open to SO_4^{-2} and H_2S may essentially be environments in which the rate of sulfate reduction is much slower than the rate SO_4^{-2} is being supplied to the system. This may be similar to the environment of deposition-precipitation alluded to by Gibson et al. [3]. In such environments, Schwarcz and Burnie [6] and Ohmoto and Rye [7] suggested k_1/k_2 values of between 1.040 and 1.060 were appropriate. In such a situation, pyrite precipitating during biogenic sulfate reduction should have $\delta^{34}S$ between -40 and -60 per mil (FIGURE 1). This model demonstrates that if the pyrite precipitated during bacterial driven sulfate reduction in a system open to SO_4^{-2}, the pyrite should be highly enriched in light sulfur (^{32}S). Differences in scale between sulfide grains and bacteria is not an important variable.

Systems closed to both SO_4^{-2} and H_2S may be analogous to a precipitation environment in which the rate of sulfate reduction is significantly faster than the rate of sulfate supply and sulfide precipitation is delayed. This delay may be a result of a limited supply of Fe (with respect to H_2S) to form pyrite. Typical k_1/k_2 values for this type of precipitation setting is 1.025 [6,7]. Ohmoto and Rye [7] demonstrated that under such settings, the $\delta^{34}S$ of the precipitating pyrite may be calculated by treating the fractionation of sulfur isotopes as a Rayleigh distillation process:

$$\delta^{34}S_{SO(t1)} = \delta^{34}S_{SO(t0)} + 1000\,(F^{(1-k1/k2)} - 1)$$

and

$$\delta^{34}S_{pyrite(t1)} = (\delta^{34}S_{SO(t0)} - (\delta^{34}S_{SO(t1)}\,F))/\,(1-F)$$

where $\delta^{34}S_{SO(t1)} = \delta^{34}S$ of SO_4^{-2} at time t,

$\delta^{34}S_{SO(t0)}$ = original $\delta^{34}S$ of SO_4^{-2},
$\delta^{34}S_{pyrite(t1)}$ = $\delta^{34}S$ of pyrite at time t,
F= fraction of SO_4^{-2} at time t.

Solving for these two equations, the $\delta^{34}S_{pyrite}$ ranges from -24.4 per mil to -4.1 per mil for F values between 0.95 to 0.05. The early pyrite will have highly negative values of $\delta^{34}S$, whereas latter pyrite will have values approaching 0 (FIGURE 1). Under this scenario, pyrite should be enriched in light S and should show a range in $\delta^{34}S$ values. Pyrite from ALH84001 that has thus far been analyzed in our lab shows neither characteristic.

In systems closed to SO_4^{-2} and open to H_2S, the rate of sulfate reduction is significantly faster than the rate of sulfate supply and H2S is continuously removed from the system by pyrite precipitation. Typical k_1/k_2 values for this type of precipitation setting is 1.025 [6,7]. Ohmoto and Rye [7] also demonstrated that this process may be treated as a Rayleigh distillation process:

$$\delta^{34}S_{SO(t1)} = \delta^{34}S_{SO(t0)} + 1000 (F^{(1- k1/k2)} - 1)$$

and

$$\delta^{34}S_{pyrite(t1)} = \delta^{34}S_{SO(t1)} - 1000 (k_1/k_2 - 1).$$

Solving for these two equations, the $\delta^{34}S_{pyrite}$ ranges from -23.7 per mil to +52.8 per mil for F values between 0.95 to 0.05. The early pyrite will have highly negative values of $\delta^{34}S$, whereas extremely late pyrite (F < 0.2) will be enriched in heavy sulfur (FIGURE 1). Under this model, pyrite should show an extremely wide range in $\delta^{34}S$ values. Pyrite thus far analyzed in our lab does not show this characteristic.

CONCLUSIONS. Based on these preliminary calculations and sulfur isotopic measurements on pyrite in ALH84001, the system represented by ALH84001 was open to SO_4^{-2}. This essential means that the rate of sulfate reduction is much slower than the rate SO_4^{-2} is being supplied to the system. This is analogous to the type of system suggested by Gibson et al. [3]. Under this scenario, if the solutions precipitating pyrite have

a $\delta^{34}S$ of approximately 0, the pyrite should be enriched in the light sulfur isotope. This is clearly not consistent with the S isotopic systematics in ALH84001. Due to the nature of the model (open system), the relative size of the pyrite in ALH84001 is not an important factor. Only three scenarios are possible: (1) The pyrite did not precipitate during biogenic activity. This scenario is currently being explored [2], (2) The solutions precipitating carbonate and pyrite were highly enriched in the heavy sulfur isotope. (3) Biogenic activity is not recorded in ALH84001.

REFERENCE. [1] Shearer et al. (1986) GCA 60, 2921-2926. [2] Shearer et al. (1997) LPSC XXVIII, this volume. [3] Gibson et al. (1996) Science 274 ,2125 [4] Thode et al. (1961) GCA 25, 150-174. [5] Rees (1973) GCA 37, 1141-1162. [6] Schwarcz and Burnie (1973) Mineral. Depos. 8, 264-277. [7] Ohmoto and Rye (1979) in *Geochemistry of Hydrothermal Ore Deposits* (ed. H.L. Barnes), 509-567.

FIGURE 1. Variation of $\delta^{34}S$ in pyrite precipitated during open-system behavior of SO_4^{-2}, closed system behavior of SO_4^{-2} and hydrogen sulfide, and closed system behavior of SO_4^{-2} and open system behavior of hydrogen sulfide. The range in pyrite for the model of open system behavior of SO_4^{-2} reflects different k_1/k_2 values. Measured values for pyrite in ALH84001 are shown for comparison.